

Boiler Maintenance & Cleaning Chemistry

Use of ammoniated citric acid for the chemical cleaning of high pressure boilers

Pre-commissional passivation Before a boiler is put into service, it is customary to follow a "pre-commissional" chemical cleaning procedure. A newly constructed boiler will be contaminated by particulate debris, oils and greases, and rust.

These are all removed in a sequence of steps, both chemical and mechanical. The resulting surface is chemically passivated to form a semi-conductive iron oxide film or layer of Fe_3O_4 . The Fe_3O_4 is a poor conductor of ions, (e.g. Fe^{2+} , Fe^{3+}) therefore protecting the steel from further corrosion. The passivating iron iii oxide is not a permanent addition to the steel. It is easily removed if water in the boiler is acidic or contains chlorides. It is also extremely thin (40 -100 Å). In fact, when viewing the grey-black colour of a passivated boiler surface, we are really seeing the true colour of the steel itself. The mechanism of passivation is thought to be as follows: Following chemical cleaning itself, the surface is that of the steel itself, with no other layers. It can therefore quickly rust in the presence of water and oxygen. The boiler is filled with a dilute citric acid solution, which dissolves this rust. The pH is raised to an alkaline value using ammonia, and the sequestered iron remains in solution. Dissolution of iron on the surface stops and an oxidizing agent is added. This has the effect of impressing a positive surface potential on the steel. In other words, it initiates oxidation of the surface to iron oxide by withdrawing electrons. As the potential increases, so does the oxidation, shown by the increase in the corrosion current. When the potential reaches about 0.6V for steel, the oxidation takes place as the formation of a semi-conductive layer of iron oxide. This layer can conduct electrons but not ions. Without a flow of ions, the steel cannot corrode and therefore the corrosion current decreases to the so-called passive current. If the potential is further increased, the corrosion current remains constant until a point when the semi-conductive layer becomes transpassive, and ionic species are conducted through it. The corrosion current will again rise and passivity is lost. For iron the value of this potential is about 1.6V. This means that by introducing an oxidizing agent to the ammonium citrate solution, which can impose a potential of between 0.6V and 1.6V on the steel surface, passivation will occur. After allowing time for the reaction, rapid draining of the solution removes the electrolyte and the steel is left in a temporarily passive state. A good choice of oxidizing agent is sodium nitrite, although sodium bromate or hydrogen peroxide can be used.

In-service conditions If filled quickly with correctly treated water, and put into immediate service, the clean boiler will be operating at maximum efficiency and will have a basic passive layer intact. Assuming good maintenance of the water supply, the boiler will operate for several years without further cleaning. During operation, the boiler is fed by de-aerated, de-mineralized water containing additives. These basically scavenge for oxygen and control the pH of the feed. By almost eliminating dissolved oxygen, while controlling pH and not overdosing additives, the boiler is kept in an optimum condition for steam production. The choice of additives to boilers is based on many years of

research. The object is always to minimize non-mobile deposits and corrosion, both of which can lead to failure. When boilers are fired up after cleaning and adding treatment compounds, a reaction occurs between the surface of the boiler and the water. Another form of iron oxide is formed. This is magnetite, or Fe_3O_4 , which is black in colour. Its formation is a complex process and can be summed up as follows: The temporary iron oxide film, only a few angstrom thick, will break down. A series of reactions occur between the iron and the water which result in the following two to form magnetite: $3\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2\text{H}_2\text{O}$ and $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$. Some intermediate reactions also produce hydrogen ions. These lower the pH of the water during start up of boilers and have to be adjusted for with additives under monitoring. Care must be taken to monitor boiler conditions. Overdosing to raise pH too much will accelerate magnetite production by removing hydrogen ions too quickly. This film will be less dense and weaker. However, if the pH is allowed to drop too far, the film is pickled away. The magnetite will continually be formed at an ever decreasing rate. Its formation can be monitored by analysing for free hydrogen. After a period of between 25000 and 40000 hours use, the magnetite film will be too thick and will require removing by chemical cleaning. It may be that during the wildly fluctuating conditions during start-up that dosage of oxygen scavengers, such as hydrazine, is too high. The excess will dissociate to form ammonia. This will react with copper in condenser components to form the soluble species $\text{Cu}(\text{NH}_3)_4^{2+}$. $\text{Cu} + 4\text{NH}_3 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{NH}_3)_4^{2+} + 2\text{OH}^-$. This reacts on return to the boiler as follows: $\text{Cu}(\text{NH}_3)_4^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+} + 4\text{NH}_3$. This is undesirable since the ammonia is recycled for further damage, while the copper corrodes the boiler. Tube scale analysis may reveal metallic copper under magnetite, with copper i oxide mixed in the magnetite in small quantities. This copper, and its oxide must be removed during cleaning, together with the magnetite.

Chemical cleaning of the boiler We have seen how a new, clean boiler can accumulate copper and magnetite which requires removal. There is a method we propose to do this. Using ammoniated citric acid and an oxidizing agent such as sodium nitrite or bromate, we will now show how this can be achieved.

1. citric acid and ammoniated citric acid Citric acid is a weak, tri-basic, organic acid. It forms complexes with iron ii, iron iii and cu i ions which are stable in solution over a wide pH range. When a citric acid solution is made up to a concentration of 3 to 5 %, its pH is between 2 and 3, i.e. It is only weakly dissociated. The process requires that the solution is partially neutralised to pH 4 using ammonia. This solution will, if heated to about 75 deg. C, dissolve iron iii oxide and magnetite, keeping both iron ii and iron iii in solution as complexes. As long as the citric concentration remains at least 3 times the dissolved iron concentration, the iron will not precipitate out as hydroxide if the solution is further treated to pH 9.5 with extra addition of ammonia. Once alkaline, an oxidizing agent is added to oxidize copper and allow it too to complex with the ammoniated citric acid: $\text{BrO}_3^- + 3\text{Cu} + 12\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow \text{Br}^- + 3\text{Cu}(\text{NH}_3)_4^{2+} + 6\text{OH}^-$ Or $2\text{NO}_2^- + 2\text{Cu} + 2\text{H}_2\text{O} + 8\text{NH}_3 \rightarrow \text{N}_2\text{O}_2^{2-} + 2\text{Cu}(\text{NH}_3)_4^{2+} + 4\text{OH}^-$. For excessive amounts of copper deposits, bromate is preferred to nitrite. A separate passivation step is unnecessary, as we have seen earlier, with the reformation of the semi-conductive iron oxide film by reaction between the steel and the oxidizing agent. For example, with bromate: $\text{BrO}_3^- + 2\text{Fe} \rightarrow \text{Br}^- + \text{Fe}_2\text{O}_3$

2. Multi-stage cleaning, with initial alkaline boil-out, followed by further stages involving citric acid, ammonium bifluoride, ammonia, a corrosion inhibitor and an oxidizing

agent. After several years in service, a boiler will have scale deposits more complex than elemental copper, copper i oxide and magnetite. typically, minerals such as serpentine ($3\text{mgo} \cdot 2\text{sio}_2 \cdot \text{h}_2\text{o}$), pectolite ($\text{na}_2\text{o} \cdot 4\text{cao} \cdot 6\text{sio}_2 \cdot \text{h}_2\text{o}$) and magnesium phosphate ($\text{mg}_3(\text{po}_4)_2$) will be present. It is therefore the job of chemical cleaning to remove all of these and revert the boiler to a (nearly) new condition. It is worth mentioning again that boiler water treatment is aimed at inhibiting development of tube scaling, modifying deposits so they are easy to remove and removing oxygen from the water. Under high operating temperatures, very tiny amounts of impurities in the boiler water will form insoluble compounds. As time progresses, these accumulate to the extent that the transfer of heat to the boiler water is impeded. Initially this is seen as an increased fuel bill, and later as failed tubes due to localized overheating. This shows that while controlled boiler water treatment is essential, the time will come when the complete removal of accumulated scale is required to "rejuvenate" the boiler.

Chemical cleaning.# initial alkaline boil-out.Although usually applied to pre-commissional chemical cleaning of new boilers for the removal of oil and grease, there is evidence, based on laboratory work and from practical experience, that a primary phase of cleaning using alkaline chemicals loosens the bond between scale and metal. The choice of alkaline compounds is wide, but to avoid the possibility of stress corrosion cracking, simple sodium hydroxide is avoided. Other salts produce hydroxyl and other useful ions without excessively high ph , for example: $\text{Na}_2\text{sio}_3 \rightleftharpoons 2\text{na}^+ + \text{sio}_3^{2-}$ sodium metasilicate $\text{Sio}_3^{2-} + 2\text{h}_2\text{o} \rightleftharpoons 2\text{oh}^- + \text{sio}_2 \cdot \text{h}_2\text{o}$ $\text{Na}_2\text{co}_3 \rightleftharpoons 2\text{na}^+ + \text{co}_3^{2-}$ sodium carbonate $\text{Co}_3^{2-} + \text{h}_2\text{o} \rightleftharpoons \text{oh}^- + \text{hco}_3^-$ $\text{Na}_3\text{po}_4 \rightleftharpoons 3\text{na}^+ + \text{po}_4^{3-}$ trisodium phosphate $\text{Po}_4^{3-} + 3\text{h}_2\text{o} \rightleftharpoons 3\text{oh}^- + \text{h}_3\text{po}_4$ At atmospheric pressures, using external equipment, a solution of trisodium phosphate with a non-ionic wetting agent is a useful alkaline cleaning solution. The mixing of trisodium phosphate with sodium metasilicate and a wetting agent has several additional advantages. Phosphate attacks calcium carbonate, releasing carbon dioxide as an effervescing gas, which also loosens other scale: $3\text{po}_4^{3-} + 5\text{ca}\text{co}_3 + 5\text{h}_2\text{o} \rightarrow \text{ca}_5(\text{oh})(\text{po}_4)_3 + 10\text{ oh}^- + 5\text{co}_2$ Silicate is able to attack magnesium sludge : $\text{Mg}_3(\text{po}_4)_2 \cdot \text{Mg}(\text{oh})_2 + 4\text{sio}_3^{2-} \rightarrow 4\text{mgsio}_3 + 2\text{po}_4^{3-} + 2\text{oh}^-$ Under other circumstances, where calcium sulphate and/or calcium silicate are present, raising the ph using sodium hydroxide can be beneficial to the cleaning: $3\text{po}_4^{3-} + 5\text{caso}_4^- + \text{oh}^- \rightarrow \text{ca}_5(\text{oh})(\text{po}_4)_3 + 5\text{so}_4^{2-}$ and $\text{Casio}_3 + 2\text{oh}^- \rightarrow \text{ca}_2^+ + \text{sio}_4^{4-} + \text{h}_2\text{o}$ The overall effect of such an alkaline cleaning step is to loosen or transform the scale to make it yield more easily when the acid cleaning is underway.

acid cleaningThe object of this phase is to remove the scale, either by total dissolution/sequestration or by making it so loose it is removed during rinsing/flushing phases. The large amounts of iron present in various forms in such scales present a separate problem of their own. It is fine to dissolve the scale and bring iron into solution. Ferric, or trivalent iron ions, however are severely corrosive to elemental iron, unless a method is used to deactivate them : $2\text{fe}^{3+} + \text{fe} \rightarrow 3\text{fe}^{2+}$ (ferric iron corrosion)To deactivate this ferric iron, it can either be reduced to ferrous, or 2 valent ions, or sequestered. Sequestering is to combine it with other species in a stable complex, which effectively remove it from the reaction equation.Inhibited citric acid and ammonium bifluorideWe have seen how ammoniated citric acid stabilizes iron and copper ions in solution as complexes, and how the copper is removed from the boiler and not re-plated by the addition of an oxidizing agent at ph of 9-10.During any acid cleaning, metallic

copper is oxidized by ferric iron to the cupric species : $2\text{Fe}^{3+} + \text{Cu} \rightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}$ This is a useful reaction, since it absorbs ferric ions and dissolves copper. It has a down side, however, if the dissolved copper is not sequestered. This will plate out on the boiler tube, while dissolving an equivalent amount of iron. $\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+}$ Cuprous oxide (copper i oxide) in boiler scale is usually present with metallic copper. This is due to the way copper i undergoes a self-redox reaction to copper and copper ii: $2\text{Cu}^{+} \rightarrow \text{Cu} + \text{Cu}^{2+}$ Thus, in an acidic boiler cleaning solution with copper and copper i oxide scale, the ingredients are there for not only ferric iron corrosion, but copper corrosion of the steel, where the corrosive copper ii ions are being regenerated. We therefore require a cleaning process which inhibits ferric iron corrosion and is quick enough to avoid excessive copper corrosion of the tubes. This is why we propose a mixture of citric acid and ammonium bifluoride, with a suitable proprietary corrosion inhibitor added.Citric acidEven without the addition of ammonia, citric acid will dissolve both ferrous and ferric oxides, forming stable complexes in solution which inhibit ferric iron corrosion. The addition of ammonia till ph of about 4 forms the species monoammonium citric acid ($\text{C}_6\text{H}_7\text{O}_7\text{NH}_4$) and diammonium citric acid ($\text{C}_6\text{H}_6\text{O}_7(\text{NH}_4)_2$). Both of these are highly effective in sequestering ferric iron, ferrous iron and cupric copper. The elemental copper is not dissolved at this point.Ammonium bifluoride, NH_4HF_2 Addition of this chemical to the citric acid contributes to the ammoniating process described above. It also has several other useful functions. It forms hydrofluoric acid in solution, which is largely undissociated. This is because hydrofluoric acid is a weak acid, with the hydrogen and fluorine components having affinity for one another. This, however, does not stop it from reacting with, amongst other things silicate scales such as acmite: $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2 + 3\text{HF} \rightarrow 2\text{FeF}_6^{3-} + 4\text{H}_2\text{SiF}_6 + 2\text{Na}^+ + 4\text{H}^+ + 12\text{H}_2\text{O}$ And ferric oxide: $\text{Fe}_2\text{O}_3 + 12\text{HF} \rightarrow 2\text{FeF}_6^{3-} + 3\text{H}_2\text{O} + 6\text{H}^+$ And magnetite: $\text{Fe}_3\text{O}_4 + 18\text{HF} \rightarrow 3\text{FeF}_6^{3-} + 4\text{H}_2\text{O} + 10\text{H}^+ + \text{e}^-$ The reason all the above take place is the stability of the hexafluoroferric ion, FeF_6^{3-} . In fact, adding ammonium bifluoride to citric acid increases dissolution of scale, both in quantity and rate, while lowering the overall corrosion of the system.Using citric and ammonium bifluoride achieves a combination of ferric ion corrosion inhibition and decreased hydrogen ion activity due to its association with free fluoride. Ammonium bifluoride can be taken to be a cathodic, or passivating inhibitor in citric acid, since it inhibits the reaction $2\text{H}^+ + \text{Fe} \rightarrow \text{Fe}^{2+} + \text{H}_2$.Corrosion inhibitorEven though ammonium bifluoride is inhibiting in nature, a corrosion inhibitor is added to the acid cleaning solution. There are 3 types of corrosion inhibitors :- cathodic, which impede the reduction of hydrogen ions-anodic, which limit oxidation of the metal, in this case iron - adsorption, forming a physical film on the metal surfaceCommercially available inhibitors are mixtures of inhibitors and other surfactants in a carrier. They are normally used following the manufacturer's instructions for the application and are extremely effective.The conclusion of the acid cleaning phase is best determined by analyzing for the two most evident components in the solution, namely dissolved iron and dissolved acid. A variety of wet and optical analytical methods are available. Following a stabilization of both acid and iron values, circulation of solutions is continued further. It is common for the values to rise to a second plateau, so cessation of cleaning immediately upon reaching initial stability is not advisable.Solutions are fully removed from the boiler and it is flushed to neutrality. When access is possible, all drums, headers and accessible tubes must be water jetted to remove loosened insoluble debris.